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Low temperature synthesis of $LaNiO_3$ perovskite *via* a dinuclear complex

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This paper reports on the synthesis and characterization of a heterodinuclear complex precursor for $LaNiO_3$ perovskite obtaining, prepared in $La(CH_3COO)_3$ – $Ni(CH_3COO)_2$ – AOH – DMF system (AOH = 2- [(diethylamino) methyl]-6-ethylphenol and DMF = dimethylformamide). According to the XRD pattern, $LaNiO_3$ obtained by calcination (700 ^{0}C, 10 minutes) of complex precursor is single phase with hexagonal perovskite-like structure. The relatively high values of specific surface area of $LaNiO_3$ samples obtained, sustain their posible catalytic activity.

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Keywords: $LaNiO_3$ perovskite, Low temperature synthesis, XRD

1. Introduction

The perovskite-type mixed metal oxides are an important class of materials with interesting physical and chemical properties. The physical properties include piezoelectricity, pyroelectricity, ferroelectricity and dielectricity which have been used in technological application like light modulation, infrared detection, charge storage, optical memory etc. The chemical properties include high catalytic activity and an oxygen-transport phenomenon [1-5].

$LaNiO_3$ – based oxides are among the most promising materials as cathodes for solid oxide fuel cells (SOFCs) and for sensors due to of their high electrical conductivity.and high catalytic activity

A limited number of papers about low temperature synthesis of $LaNiO_3$ by different routes have been reported in the relevant literature: sol-gel procedure, inverse microemulsion technique or calcination of heteronuclear complexes [6,7].

A common aim of the above methods is to decrease the interatomic distances between the adjacent cations in order to minimize the diffusion limitations, which merely control the formation of the final solids.

A method that overcomes the above limitations may be that employs dinuclear complexes in which the metallic cations are held together in neighbouring sites through oxygen bridges. Homogenous mixed oxides with relatively high specific surface area are formed at low temperatures when heteronuclear complexes are used as precursors.

Our paper proposes the use of a new dinuclear complex $[LaNi(AO)_2(CH_3COO)_3]$ (AOH = deprotonated 2- [(diethylamino) methyl]-6-ethylphenol) as a precursor for $LaNiO_3$ perovskite oxide synthesis.

The choice of an aminophenol as ligand in a heterodinuclear complex precursor has been determined by the capacity of such ligands to generate not only mononuclear complexes (sometimes of unusual stoichiometries and stereochemistries) but also, a lot of polynuclear complexes in which the oxygen atom from the deprotonated phenolic group acts as a bridge joining the different monomeric entities [8,9].

The dinuclear complex has been characterized by molar electrical conductivity measurements, electronic and FT-IR spectra, TG/DTA analysis and $LaNiO_3$ obtained by the calcination of the precursor has been characterized by X-ray diffraction patterns, SEM and surface area measurements.

2. Experimental procedure

Synthesis of the complex precursor, $LaNi(AO)_2(CH_3COO)_3$

A mixture of $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.25g, 0.01mol), $La(CH_3COO)_3$ (0.316g, 0.01mol) and 2-[(diethylamino)-methyl]-6-ethylphenol (0.414g, 0.02mol) in DMF (15mL) was refluxed for 5 hours at 40-50 ^{o}C. The yellow-greenish solution obtained was evaporated at room temperature during few days. The light brown crystals formed were collected by suction filtration, washed successively with distilled water, methanol and diethyleter and dried on P_4O_{10} in a dessicator.

Elemental chemical analysis

LaNi $C_{32}H_{51}N_2O_8$: calc. La %, 17.72; Ni%, 7.48; N %,3.57; C %, 48.94; H%, 6.48.

found: La%, 17.53; Ni%, 7.80; N%, 3.95; C%, 49.80; H%, 6.95.

Molar electrical conductivity measurements

Molar conductivity measurements have been recorded on OK 102/1 Radelkis conductometer on 10^{-3} M solution in DMSO.

Spectral studies

UV-Vis spectra were recorded on a VSU-2G spectrophotometer using MgO as standard sample and FT-IR spectra on a Perkin Elmer spectrophotometer with samples prepared as KBr pellets.

Thermodifferential studies

The obtained complex was studied with a Paulik Paulik-Erdey derivatograph with simultaneous recording of T, TG, DTG and DTA signals curves. The measurements were carried out in a flow of 10 cm^3 min^{-1} of atmospheric air, with calcined α-Al_2O_3 as a blank and rate heating.of 5^{0}C/min

XRD studies of the thermal decomposition products

XRD patterns were recorded on a Siemens D 500 diffractometer (CuK$_\alpha$ radiation, λ=1.54056 Å).

BET Surface area

The specific surface area was measured by the one-point BET method using as gas adsorbed N_2 at 77 K in a Carlo Erba Sorpty 1750 apparatus.

3. Results and discussion

Characterization of the dinuclear complex precursor

The dinuclear complex, $[LaNi(AO)_2(CH_3COO)_3]$ was obtained in DMF solutions using Ni(II) and La(III) acetates and as ligand an aminophenol. The proposed formulae of the complex was supported by elemental chemical analysis and molar conductivity measurements, the compound being of nonelectrolyte type.

Table 1. Molar electrical conductivity and UV-Vis spectral bands.

Molar conductivity Ω-1cm^{2}mol^{-1} (Type of electrolyte)*	UV-Vis spectrum	
	Bands (nm)	Assignment
35 nonelectrolyte	420 660	1A1g → 1B1g (a1g → b1g) 1A1g → 1A2g (b2g → b1g)

* solution 10^{-3}M in DMSO

The diffuse reflectance spectrum of dinuclear complex precursor (Fig. 1a) presents in UV-Vis range, two characteristic bands for Ni (II) (d^8) ion in a square planar geometry with the assignment indicated in Table 1.The absence of bands over 1000 nm sustains square planar geosmetry of the complex.[10].

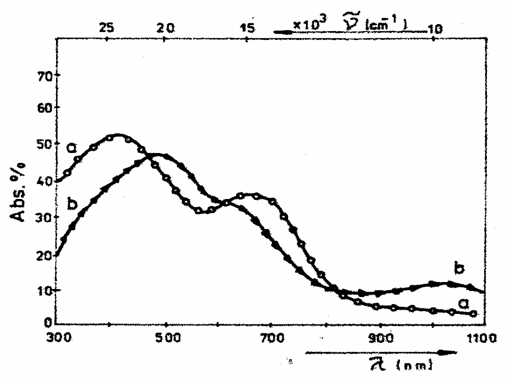

Fig. 1. The electronic spectra of : (a) dinuclear complex $[LaNi(AO)_2(CH_3COO)_3]$ $LaNiO_3$ obtained from (a) by calcination at 700 ^{0}C , 1 h.

The IR spectrum of dinuclear complex precursor was registered in comparison with the spectrum of the free aminophenol ligand (Fig. 2a and b).

From their comparison, some important conclusions on the ligand coordination were obtained:

- the absence of ν_{OH} frequency (3400-3500 cm^{-1}) in the spectrum of the complex is a proof of the ligand coordination through deprotonated OH phenolic group;
- the shifting of $\nu_{C\text{-}O}$ and $\nu_{C\text{-}N}$ frequencies (at 1180cm^{-1} and 1260cm^{-1} respectively, in the ligand spectrum) to lower values (1120 cm^{-1} and 1210 cm^{-1}, respectively) in the spectrum of the complex is very probable a consequence of the coordination through oxygen of the deprotonaited phenol group and N-alkilated groups.
- in the IR spectrum of the complex the two bands, at 1580 cm^{-1} ($\nu_{as/OCO}$) and 1410 cm^{-1} ($\nu_{s/OCO}$) were assigned to the bidentate coordination of acetate anions [11].

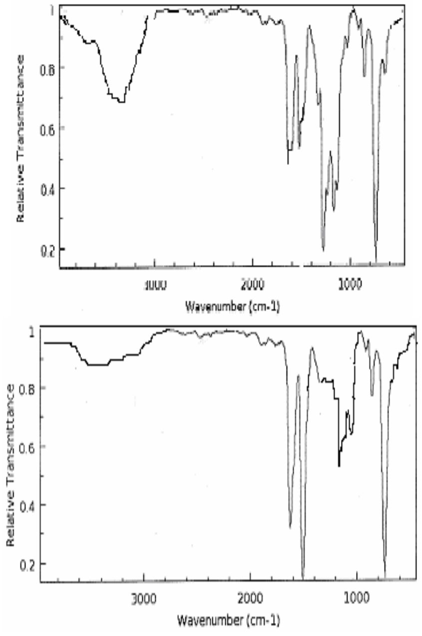

Fig. 2. IR spectra of : (a) aminophenol ligand; (b) dinuclear complex precursor.

The thermal decomposition of $[LaNi(AO)_2(CH_3COO)_3]$ complex was studied in order to establish the best conditions for pure $LaNiO_3$ obtaining (Fig. 3). The decomposition in steps of the complex started at about 120 ^{o}C with three weight losses, partially overlapped (an abrupt weight loss begining at around 300 ^{o}C was followed by two slower losses that ended at about 600 ^{o}C).

The DTA curve showed one endothermic peak around 180 ^{o}C(with acetate elimination) and three exothermic peaks corresponding to the ligand oxidation and to the formation and crystallization of $LaNiO_3$.

The weight loss percentage 68.85 wt % in the last plateau range (~620 ^{o}C) was in good agreement with theoretical value of 68.70 wt % calculated by assuming the formation of $LaNiO_3$ from the complex with the $[LaNi(AO)_2(CH_3COO)_3]$ formulae.

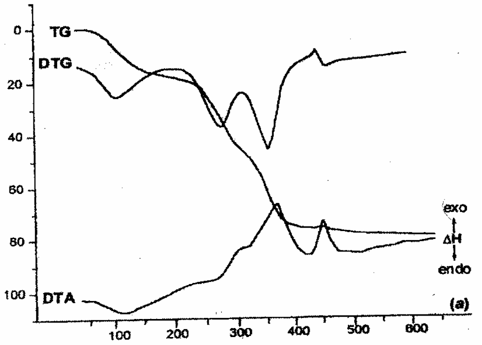

Fig. 3. Thermodifferential analysis of dinuclear complex precursor.

The estimation of electron densities by molecular orbital calculations confirms our experimental data and supposition regarding the structure of the complex (Fig. 4).

The high values of electronic densities on OH-phenolic group and on N-alchilated amino groups of AOH ligand and the calculated N…O distance (3.2293 A) confirm the bidentate nature of the ligand and are in good agreement with our supposition about the geometry of the complex precursor.

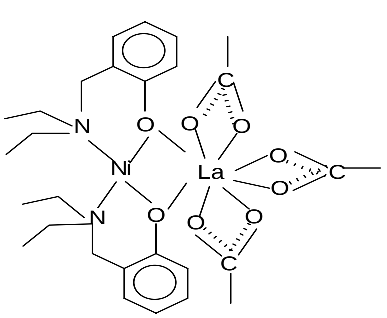

Fig. 4. The proposed structural formulae for dinuclear complex.

$LaNiO_3$ characterization

Fig. 5 shows the XRD analysis of dinuclear complex precursor calcinated at 700 ^{o}C, 10 min and 700 ^{o}C, 1 hour.

The XRD patterns for the samples fired at 600 ^{o}C showed diffuse bands typical of amorphous phase. In contrast, the XRD patterns for the complex precursor decomposed at 700 ^{o}C and especially at 800 ^{o}C showed clearly an hexagonal $LaNiO_3$ perovskite type structure.

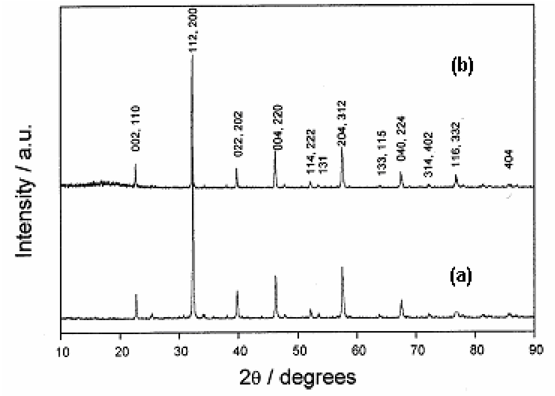

Fig. 5. XRD power diffraction patterns of samples obtained by calcination of precursor at 700 ^{0}C (a) 10 minutes; (b) 1 hour.

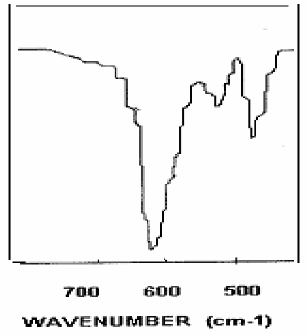

Fig. 6. IR spectrum of $LaNiO_3$ obtained by calcination at 700 ^{0}C, 1 h.

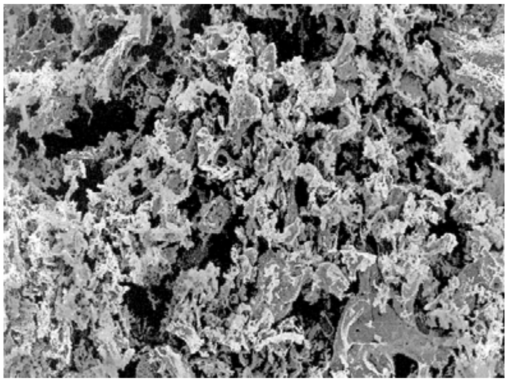

Fig. 7. SEM imagine of $LaNiO_3$ obtained by calcination at 700 ^{o}C, 1 h.

The reflectance UV-Vis electronic spectrum of the product obtained by the calcination of the complex precursor at 700 ^{o}C (1h) (Fig. 1b) was completely different than that of the initial complex and indicated the presence of Ni(III) (d^7) in a strong distorted octahedral symmetry (three bands at 490 nm, 660 nm and 1050 nm respectively were observed).

The IR spectrum of this product presented only the characteristic bands for $LaNiO_3$, namely two bands in 450-500 cm^{-1} range and one band at 620 cm^{-1}, corresponding to the stretching vibrations of the La-O and Ni-O-La bonds, respectively.

According to the XRD pattern, $LaNiO_3$ obtained from the decomposition of complex precursor at 700 °C (1h) was single phase with hexagonal perovskite type structure: a = b = 5.460 Å; c = 6.575 Å. These values are in good agreement with the data given in the literature, i.e. a = b = 5.457 Å; c = 6.572 Å (reference JCPDS file no. 33-0711).

The XRD results showed that the mixed oxide was directly formed from the precursor after the decomposition of organic ligand, without formation of intermediate crystalline compounds. This allows the synthesis of $LaNiO_3$ *via* dinuclear complex at low temperature.

In Fig. 6 was presented SEM image of a $LaNiO_3$ sample obtained from the complex precursor calcinated at 700 °C, 1 hour.

The value of surface area for $LaNiO_3$ obtained in this paper was compared with those determined for pure and doped perovskites ($LaNiO_3$ or $LaCoO_3$) obtained by other methods.

Table 2. The values of surface area for some perovskites obtained by calcination of complex compounds.

Samples	Preparation conditions	Surface area (m^2/g)
$LaNiO_3$ obtained in this paper	650 °C; 2 h 700 °C; 10 min	35.8 34.2
$LaNiO_3$ [12]	600 °C ; 1 h 700 °C ; 1 h	9.4 9.1
$LaCoO_3$ [6]	800 °C, 3 h	27
$La_{0.9}Sr_{0.1}CoO_3$ [6]	1000 °C; 4 h	29.4

4. Conclusions

Single-phase, hexagonal perovskite-like structure $LaNiO_3$ was prepared by the thermal decomposition of a new dinuclear complex, $LaNi(AO)_2(ac)_3$ at low temperature.

The high values of the surface area of $LaNiO_3$ powders prepared by this method make them promising materials for the application as electroceramics materials or catalysts.

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